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PRODUCTION AND PHYSICAL METALLURGY

OF PURE METALS -- PART VI

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PRODUCTION AND PHYSICAL METALLURGY
OF PURE METALS -- PART VI

Electronographic and Kinetic Investigation of the
Process of Oxidation of Zirconium and Certain
Alloys on its Base

Following is a translation of an article by
I. I. Korobkov, D. V. Ignatov, A. I. Yevstyukhin
and V. S. Yemel'yanov in Metallurgiya i Metall-
ovedniye Chistykh Metallov (Production and Physical
Metallurgy of Pure Metals), No. 1, Moscow, 1959,
pages 144-161.⁷

In connection with the use of zirconium and of some of its alloys in nuclear reactors, great attention has been paid recently to the physicommechanical properties of pure zirconium and its alloys. The mechanics of oxidation of zirconium and its alloys in pure oxygen, air and steam have also been studied, as well as the structure and composition of the scale. Certain articles describing different modifications of zirconium oxides, temperature areas of their stability, and certain state diagrams of zirconium oxides with other metals have already been published. Basic work on the oxidation of zirconium and its alloys is contained in the monographs /1/ and /2/ and articles /3/ through /9/. One of the fundamental flaws of this work resides in the fact that the studies of the oxidation kinetics of zirconium were not appropriately tied in with the work determining the structure and composition of oxide films formed on the surface at different temperatures and over different heating times.

The present work contains the results of an investigation of the oxidation kinetics, structure and composition of oxide films formed on the surfaces of specimens of zirconium and of its alloys heated in oxygen and in air at temperatures ranging from 20 to 800°C.

Experimental Part

The structure and composition of oxide films were determined by electronographic /electron diffraction/ methods. The kinetics of oxidation in oxygen were investigated by means of continuous weighing on a vacuum torsion microbalance with a sensitivity of 10^{-6} g. Studies of kinetics in the air were carried out by intermittent weighing on ordinary micro-analytical scales with a sensitivity of 10^{-5} g per division on the optical scale of the cathetometer.

The first tests showed that oxidation kinetics and the structure and composition of oxide films were substantially the same whether the zirconium specimens were oxidized in air or in oxygen over the temperature range of 200 to 500°C. In the 500 to 800° range weight increases of specimens subjected to oxidation for long periods (15-20 hr) were so great that ordinary scales with a sensitivity of 10^{-5} g were fully adequate. In such cases, by using massive specimens (15 X 10 X 3 mm) one could determine the structure and composition of oxide films from electronograms obtained after heating at prescribed temperatures and times. It was possible to compare the structural data with the oxidation speed for separate points or sections of the kinetic curve. Thus the same specimens were used for kinetic and electronographic (reflection) studies. The surfaces were smoothed with emery paper (from coarse grades down to 4/0). After honing, the specimens were rubbed with purified acetone or absolute alcohol.

Heating of samples (in air) was done in an electric muffle furnace, the temperature of which was determined by a thermometer with an accuracy of $\pm 10^{\circ}$.

Reflection electronograms frequently show lines which are not sufficiently sharp, due to a strong background; therefore the structure and composition of surface films were tested additionally by transmission electronograms. In such cases, thin films (300-400 Å) of zirconium and its alloys with Al, Ti and Sn prepared by evaporation and condensation under high vacuum (10^{-7} mm Hg) were used as specimens.

Specimens were prepared from iodide (doubly refined) and iodide zirconium remelted (in an arc furnace with cooled copper anode and tungsten cathode). The percentage chemical composition of zirconium was as follows:

Zr - 99.9; W - 0.01; Ni - 0.001; Cr - 0.03; Fe - 0.002;
Ca - 0.005; C - 0.05; Hf - 0.05; Mn - 0.002; N - 0.004;
Ti - 0.0034; Cu - 0.001; Mo - 0.01.

Results and Discussion

The results of the electronographic investigation of thin oxide films on zirconium and zirconium alloyed with Al (6 and 12 wt-%), Ti (6.12 and 20 wt-%) and Sn (15 wt-%) permitted the deciphering of reflection electronograms recorded for massive specimens, and are of great independent importance as well for understanding the mechanics of oxidation of zirconium and its alloys. For this reason the report on the results of investigation begins with the description of electronographic analytical data.

Polymorphic conversions of ZrO_2 in thin films

Fig. 1 (a-f) shows electronograms of thin zirconium films heated in air at 18 to 1100°C. Calculation from the electronogram in Fig. 1 a shows that at room temperature no oxide film of a thickness detectable by electron diffraction is formed on zirconium. However, the values of interplanar distances (for α -zirconium) as determined for zirconium film electronograms are greater by 2% than those obtained from radiograms. This increase in interplanar distances apparently can be explained by the fact that such films, when removed from vacuum and separated from the substratum, are saturated with oxygen which, as we know, can be dissolved in α -zirconium up to 40 atom-percent [1], the atoms (or ions) of dissolved oxygen penetrating between the nodes of the α -Zr lattice.

Data calculated on the basis of the 270° zirconium film electronogram showed that the film was fully oxidized; calculated values of interplanar distances (d_{hkl}) coincided well with d_{hkl} values for the cubic modification of zirconium oxide (ZrO_2) with a lattice constant $a = 5.09 \text{ \AA}$ (in the presence of one surplus line corresponding $d = 2.10 \text{ \AA}$).

The somewhat increased line width in Figs. 1 a and 1 b indicates that both ZrO_2 and α -Zr consist, in this case, of small crystals.

Upon further heating of the specimen to 1300°, diffraction rings on the electronograms became sharper, and interplanar distances calculated therefrom corresponded to:

- (a) the above-mentioned cubic modification
- (b) in the range between 270 and 650°, tetragonal zirconium oxide (ZrO_2 with lattice constants $a = 0.07 \text{ \AA}$),

$c = 5.16 \text{ \AA}$ and $c/a = 1.02$ (Fig. 1c) (+);

(c) between 650 and 750° ; a mixture of tetragonal and monoclinic zirconium oxide,

(d) between 750 and 1100° ; monoclinic zirconium oxide only (ZrO_2) with lattice constants $a = 5.17 \text{ \AA}$, $b = 5.26 \text{ \AA}$, $c = 5.30 \text{ \AA}$, and $\beta = 80^\circ 48$.

Thus electronographic analysis established that
- between 1100 and 1300° a thin zirconium film heated to 270° in air is fully oxidized and cubic ZrO_2 is formed, which under further heating is subject to polymorphic transformation of the monotron type, the cubic lattice being stretched along one of its axes, becoming tetragonal. At temperatures of 750° and higher the latter is further deformed into a monoclinic lattice similar to the deformed CaF_2 lattice.

By heating thin films of cubic ZrO_2 over the same temperature ranges in oxygen (at 100 mm Hg) and under vacuum (in the electronograph itself at a residual gas pressure $P = 10^{-4} \text{ mm Hg}$), the same sequence of polymorphic transformation was observed as when the films were heated in air. Thus, these transformations are not due to any additional oxidation.

Analogous polymorphic transformations of ZrO_2 were observed in oxide films on massive specimens of zirconium heated in oxygen and in air from 300 to 800° . In this case, however, the transformation of the cubic ZrO_2 into the tetragonal was difficult to follow owing to the slight difference in the lattice constants of these oxide modifications (for cubic ZrO_2 , $a = 5.09 \text{ kX}$; for tetragonal ZrO_2 , $a = 5.07 \text{ kX}$ and $c/a = 1.02$); smudged diffraction lines and a strong background of incoherent electron scattering in the reflected electronograms presented additional difficulties. The transformation of tetragonal ZrO_2 into the monoclinic form depended on the temperature and heating time, and occurred only at a certain film thickness for a given temperature, the thickness decreasing as the temperature increased from 700 to 800° . Thus at 700° the thickness was $2.6 \cdot 10^{-3} \text{ cm}$, while at 800° it was $2 \cdot 10^{-3} \text{ cm}$. The thickness at which transformation of tetragonal ZrO_2 into monoclinic ZrO_2 takes place is called hereafter the critical

(+) The appearance of the tetragonal modification of ZrO_2 is apparent on the electronogram as the doubling of some lines, as, for example, that of the atomic plane with index (002) (see Fig. 1c).

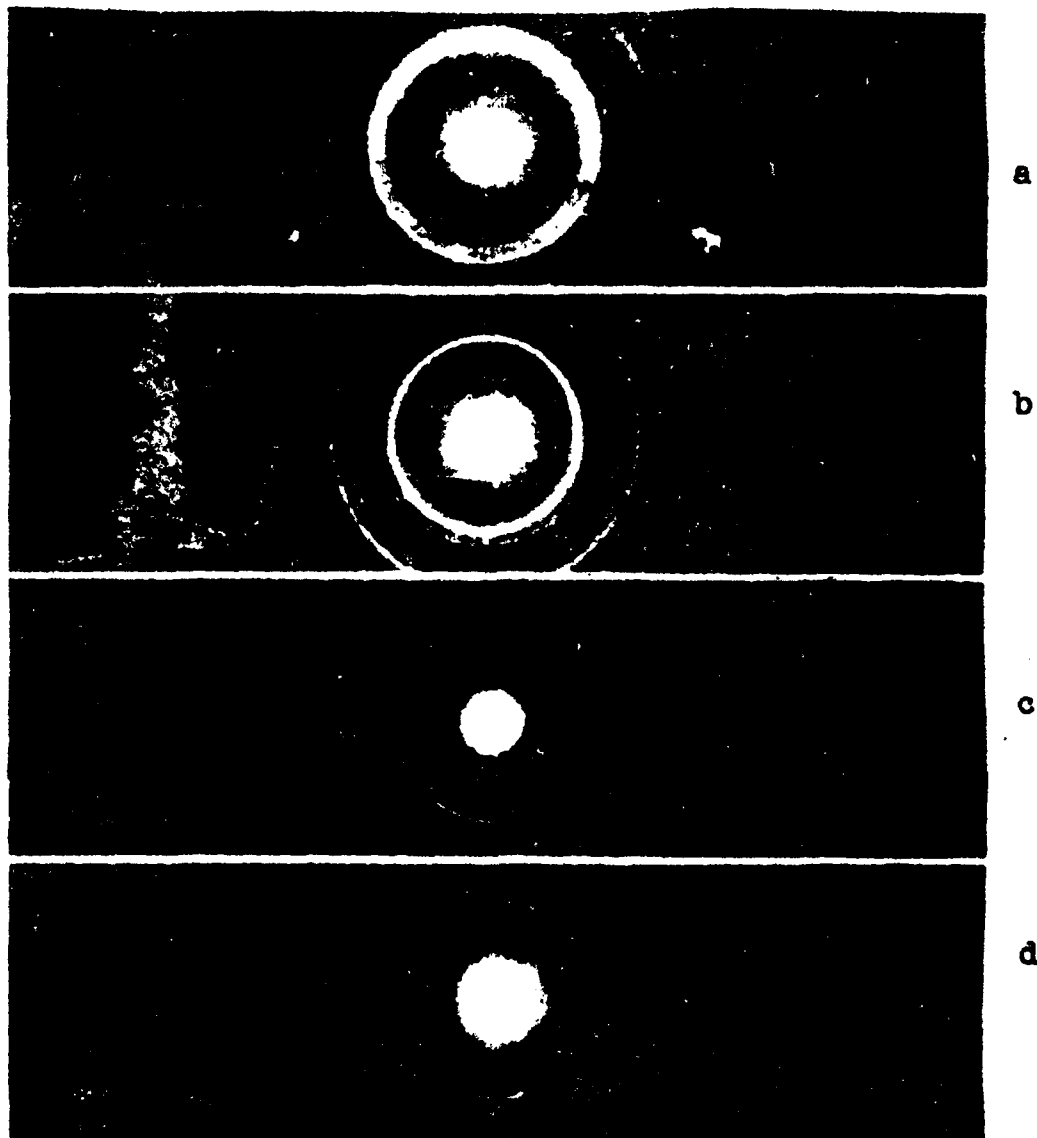


Fig. 1 [see legend on page 6]

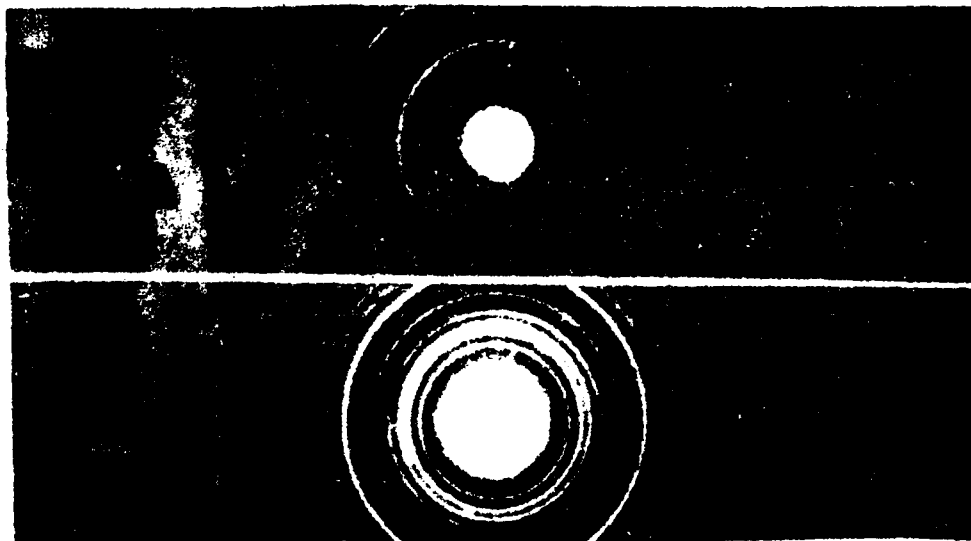


Fig. 1 Electronograms of thin zirconium films
heated in the air.

thickness. It appears from the analysis of the oxidation kinetics that at this thickness, not only is there a structural transformation of the oxide scale lattices, but also the speed of oxidation rises considerably and follows a linear law instead of a parabolic law as previously.

In Fig. 2a is shown an electronogram recorded for a massive polished zirconium specimen, without heating; Fig. 2b is the electronogram of the same specimen heated in the air for one hour at 400° . Electronograms of the same type were obtained in all cases where the surface oxide film was dark blue. Upon transformation from tetragonal ZrO_2 is shown. The electronogram was obtained from a powder by the transmission method (a layer of white ZrO_2 was removed from the surface and ground into powder). In Fig. 2d the reflection electronogram of an oxidized zirconium specimen and the transmission electronogram of an Al standard are shown together (+).

The influence of Ti, Al and Sn additives on polymorphic transformations of zirconium dioxide. Thin-film specimens of zirconium alloys with Ti, Al and Sn were heated in air at temperatures ranging from 300 to 1100° , and transmission electronograms were taken after each heating. It was found that Al additions (5 wt-%) or Ti additions (6 wt-%) stabilize the cubic ZrO_2 formed during the oxidation within the above-mentioned temperature range. In addition, the introduction of these metals did not result in the formation of independent oxidized aluminum or titanium phases. The lattice constant of cubic ZrO_2 did not change because of aluminum addition, whereas the addition of titanium resulted in a decrease of a to 5.06 Å.

Electronograms of a zirconium alloy with 10 wt-% Al and 12 wt-% Ti showed, in addition to the reflection of cubic ZrO_2 , the lines corresponding to γ - Al_2O_3 (up to 600°), as well as TiO_2 .

The addition of tin to zirconium, up to 15 wt-%, had no substantial influence on the polymorphic transformation of zirconium dioxide over the whole temperature range (300 to 1100°).

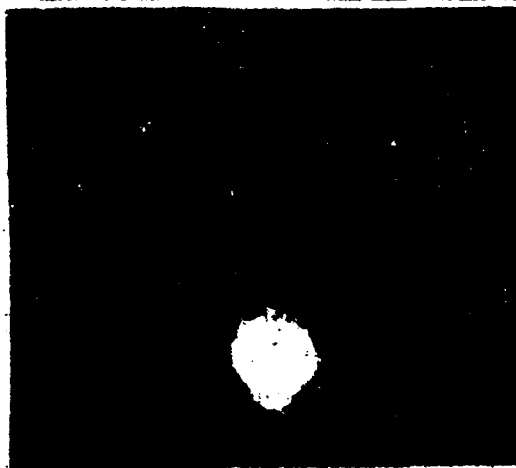
Fig. 3 shows electronograms of zirconium alloy samples heated to $1000^{\circ}C$.

Thus, aluminum oxides -- Al_2O_3 with $a = 3.95$ Å and Al_2O_3 with $a = 7.90$ Å -- as well as titanium oxide --

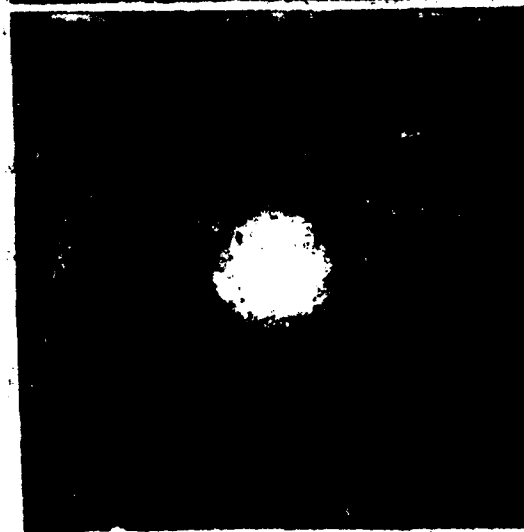
(+) The instrument constant (2 L) for the reflection electronograms was determined by a transmission electronogram of a thin aluminum film, obtained simultaneously with the reflection electronogram.



a



b



c

Fig. 2 [see legend on page 9]



d

Fig. 2 Electronograms of massive zirconium specimens: a) unheated; b) heated in the air at 400° for 1 hr; c) white oxide film; d) specimen heated to 400°C and thin Al film.

TiO₂ (rutile) and probably TiO with $a = 4.24 \text{ \AA}$ -- form limited solid solutions with cubic ZrO₂ and stabilize it in the temperature range of 300 to 1100°. SnO₂ does not react in this temperature range with oxide modifications of zirconium, i.e., it does not form solid solutions or compounds with them.

The results of kinetic studies of zirconium oxidizability in the air in the temperature range of 300 to 800° are shown in Fig. 4. From an analysis of the curves it follows that at 300 to 400° the process of oxidation follows an exponential law and, practically speaking, ceases after two hours. At 400 to 500° the oxidation proceeds at rather logarithmic $\sqrt{y} = k \log (at + 1)$ and then cubic $\sqrt[3]{y} = kt + t/\text{rates}$. In the temperature range of 575 to 800° the oxidation curves, until the oxide film attains the critical thickness, follow a parabolic law $\sqrt{y^2} = kt + c$, whereas above the critical thickness, it follows approximately a linear law $\sqrt{y} = kt + c$. This conclusion concerning the movement of kinetic curves is clearly apparent from graphs of Fig. 5, plotted in coordinates corresponding to each oxidation law.

From the linear plots of the parabolic oxidation law (Fig. 5) it follows that these straight lines have two different slopes for each temperature, depending on the duration of the heating period.

The constants of the parabolic law of oxidation, calculated in accordance with the tangents of these angles, are given in the table.

From this table it appears that the rates of oxidation are higher in the initial than in the later period, within the parabolic range. Such a difference in the rate of oxidation, depending on the elapsed oxidation time, has been observed by many authors (*) and reviewed in detail by Gulbransen in particular /10/. In addition to the five factors noted by Gulbransen (change in surface area of the specimen, rise of temperature due to heat of formation, change in crystal size, etc.) influencing the rate of oxidation in the first stage of the process, let us point out that the modifications of the oxides from one form to another may also have an effect.

In our case, for instance, there probably occurs a transformation of cubic ZrO₂ into tetragonal, and of the latter partially into monoclinic as evidenced in electronograms by weak reflections from monoclinic ZrO₂, along with reflections from tetragonal ZrO₂, on the surface of oxidation. (*) Observed for the first time by N. V. Ageyev during prolonged oxidation of nickel specimens /11/.

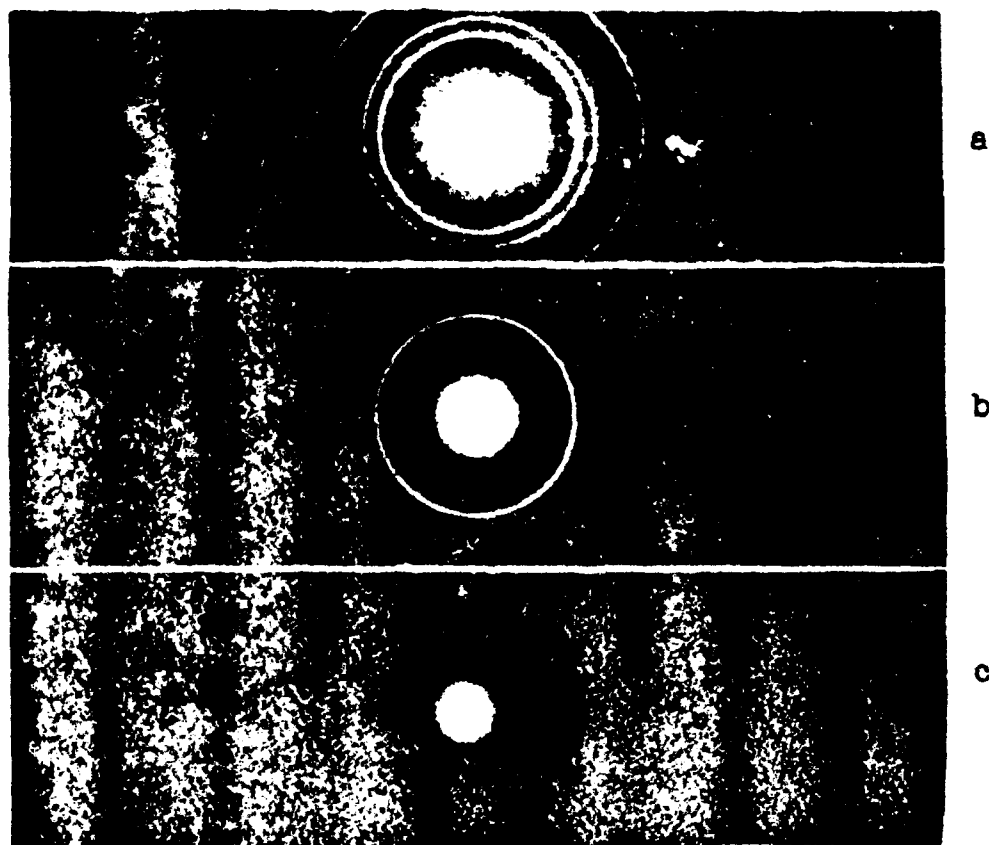


Fig. 3. Electronograms of thin zirconium alloy films heated to 1000°C:
a - 10% Al; b - 20% Ti; c - 15% Sn.

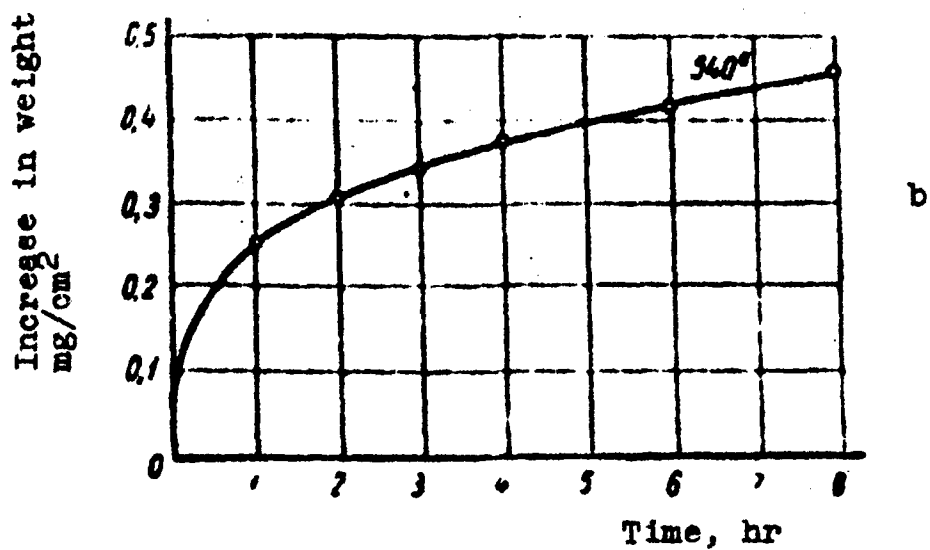
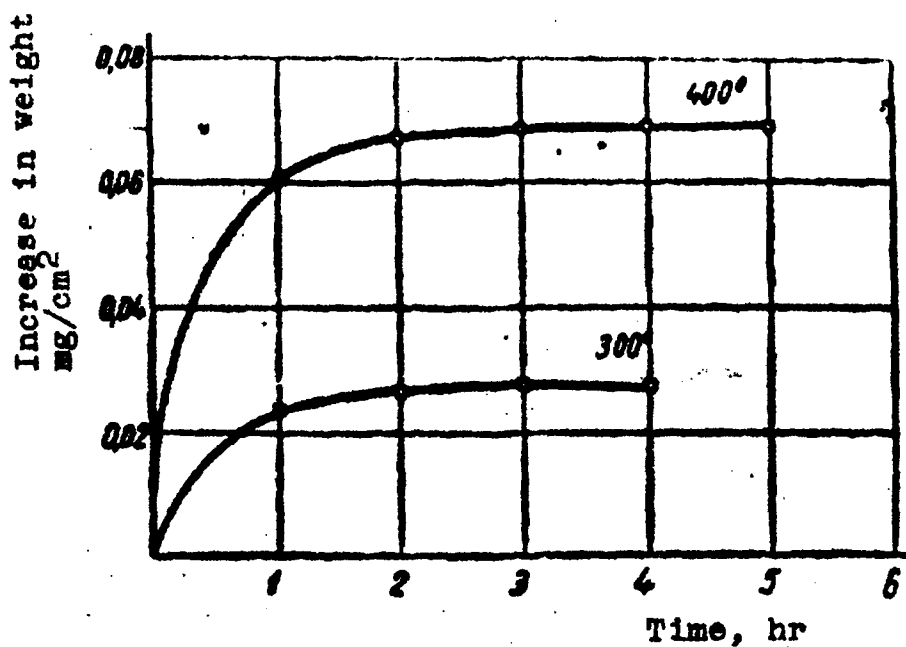
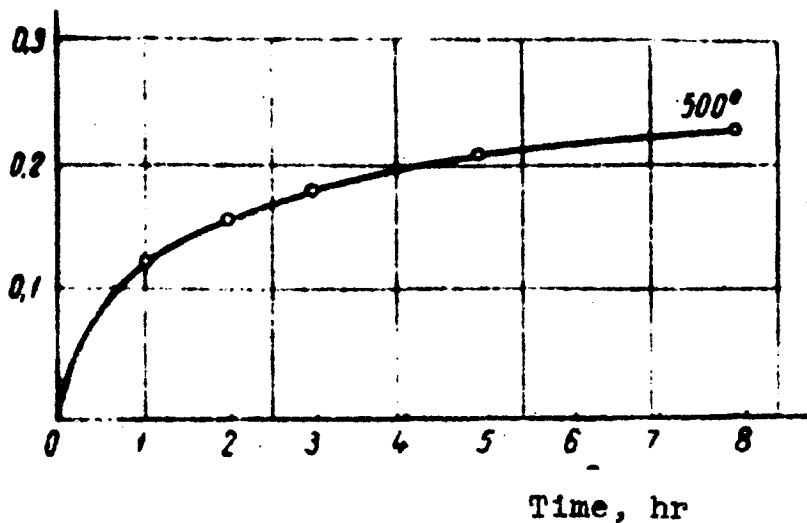


Fig. 4. Curves of zirconium oxidation in the temperature range of 300 to 800°C.

Increase in weight,
mg/cm²



Increase in weight,
mg/cm²

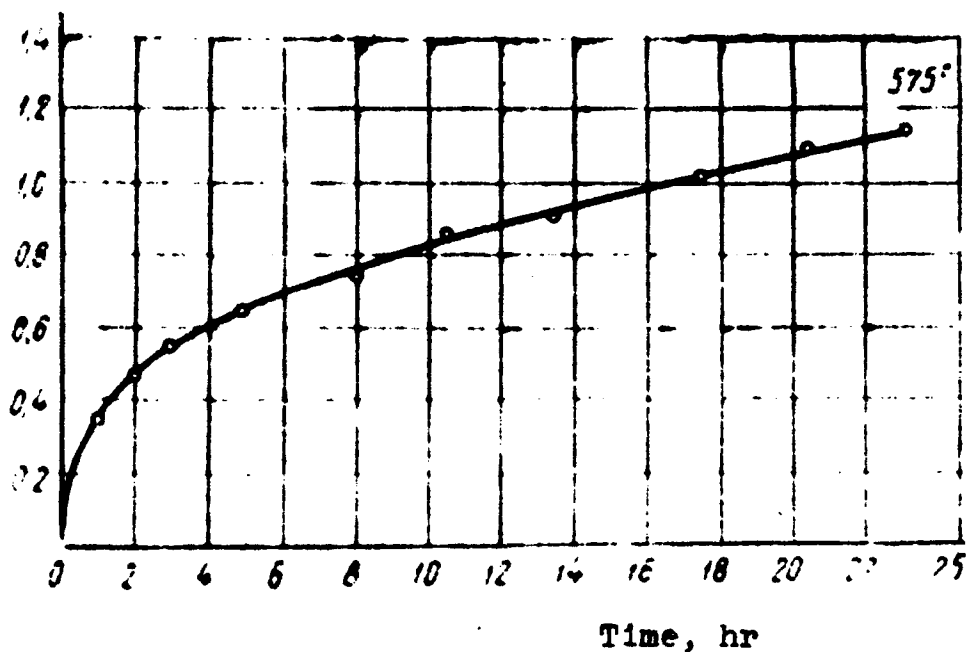


Fig. 4. Curves of zirconium oxidation in the temperature range of 300 to 800°C.

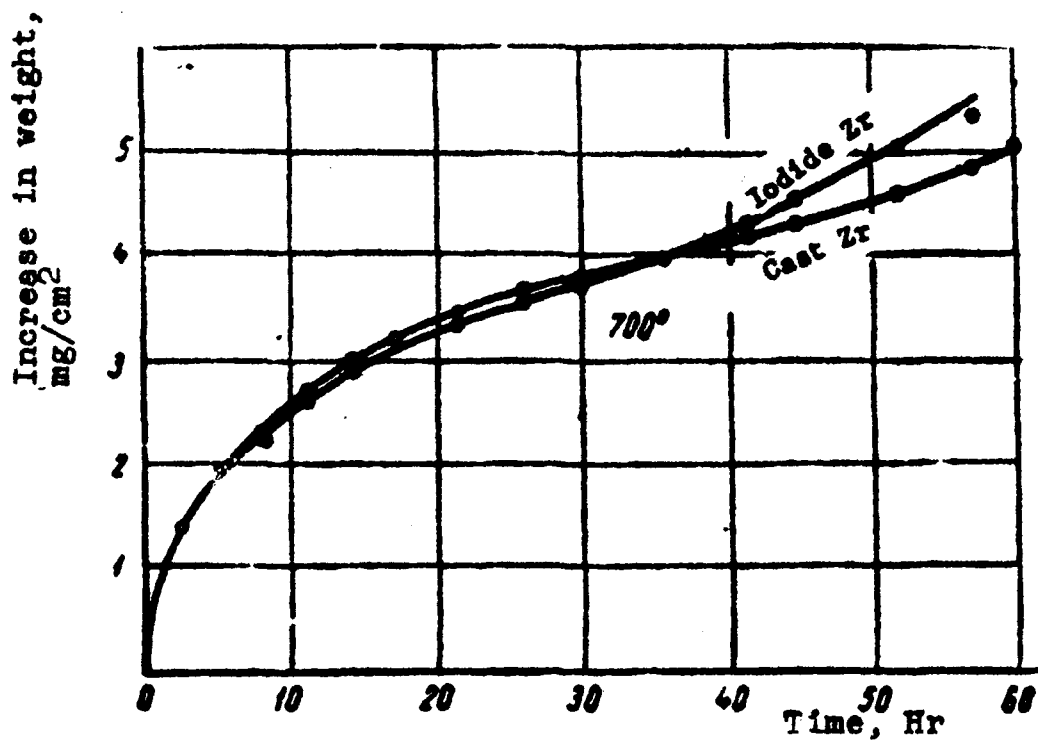
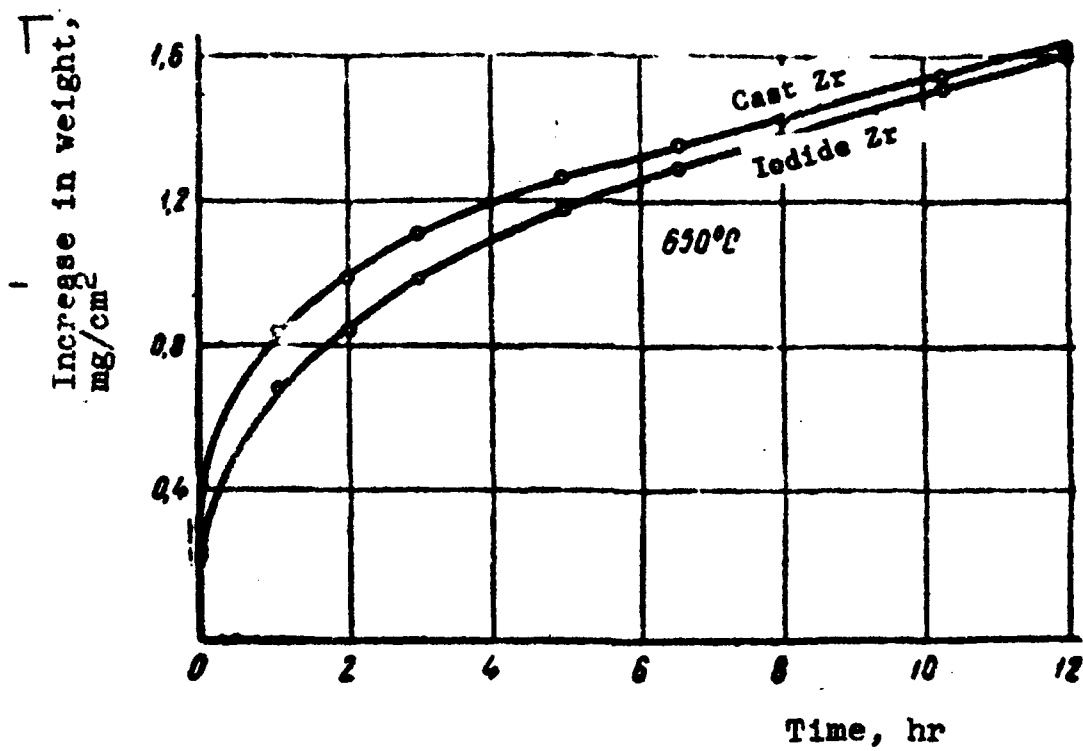


Fig. 4. Curves of zirconium oxidation in the temperature range of 300 to 800°C.

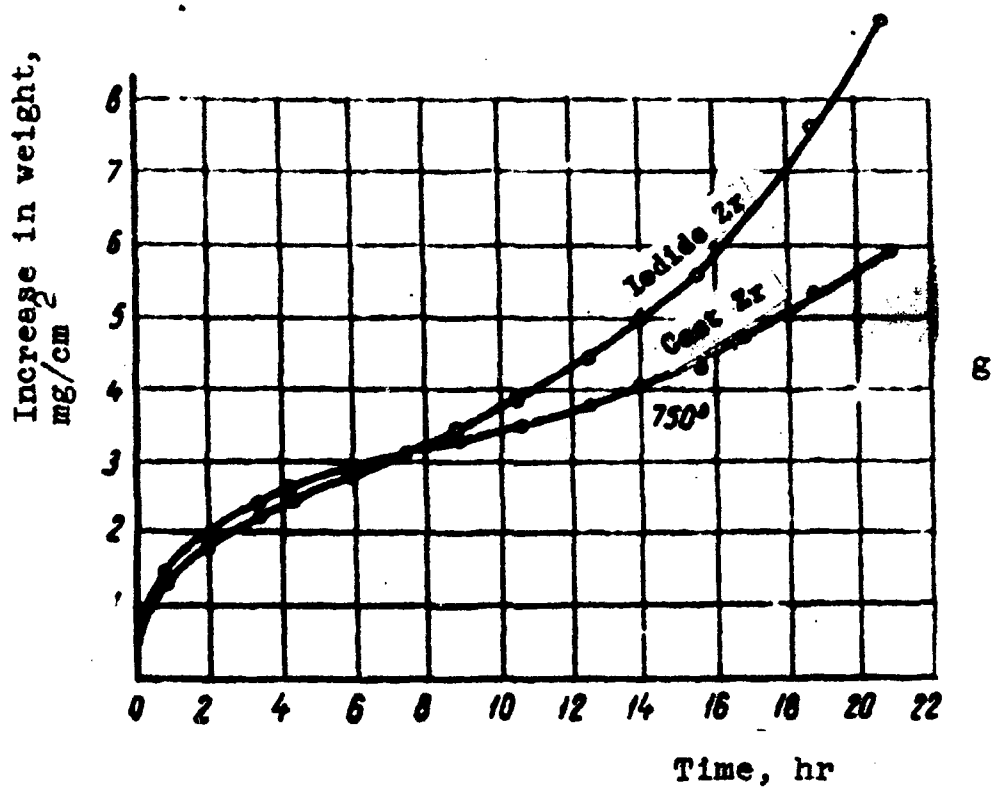


Fig. 4 Curves of zirconium oxidation in the temperature range between 300 and 800°C.

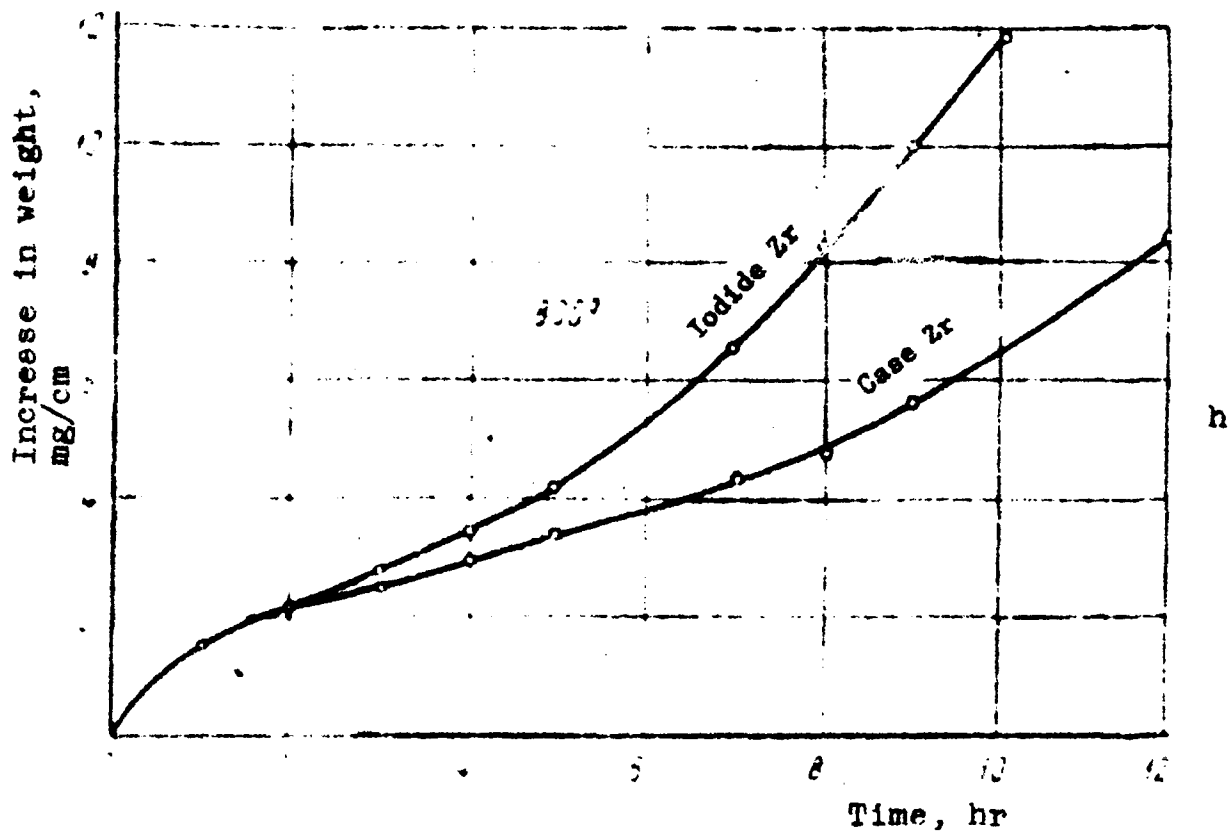


Fig. 4 [Continued from pages 12 through 15].
Curves of zirconium oxidation in the temperature range between 300 and 800°C.

Table

Values of the constants k of the parabolic law
of oxidation in $(g/cm^2)^2/sec$ for iodide-and
cast zirconium

T, °C	575°		650°		700°		750°		800°	
	up to 5 hr	over 5 hr	up to 3 hr	over 5 hr	up to 17 hr	over 21 hr	up to 4.5 hr	over 6 hr	up to 3 hr	
Iodide	$2 \cdot 10^{-11}$	$1.42 \cdot 10^{-11}$	$7.38 \cdot 10^{-11}$	$3.25 \cdot 10^{-11}$	$1.39 \cdot 10^{-10}$	$8.77 \cdot 10^{-11}$	$3.33 \cdot 10^{-10}$	$3 \cdot 10^{-10}$	$6.1 \cdot 10^{-10}$	
Melted	$2 \cdot 10^{-11}$	$1.42 \cdot 10^{-11}$	$7.38 \cdot 10^{-11}$	$3.24 \cdot 10^{-11}$	$8.8 \cdot 10^{-11}$	$5.2 \cdot 10^{-11}$	$3.33 \cdot 10^{-10}$	$2.39 \cdot 10^{-10}$	$6.1 \cdot 10^{-10}$	

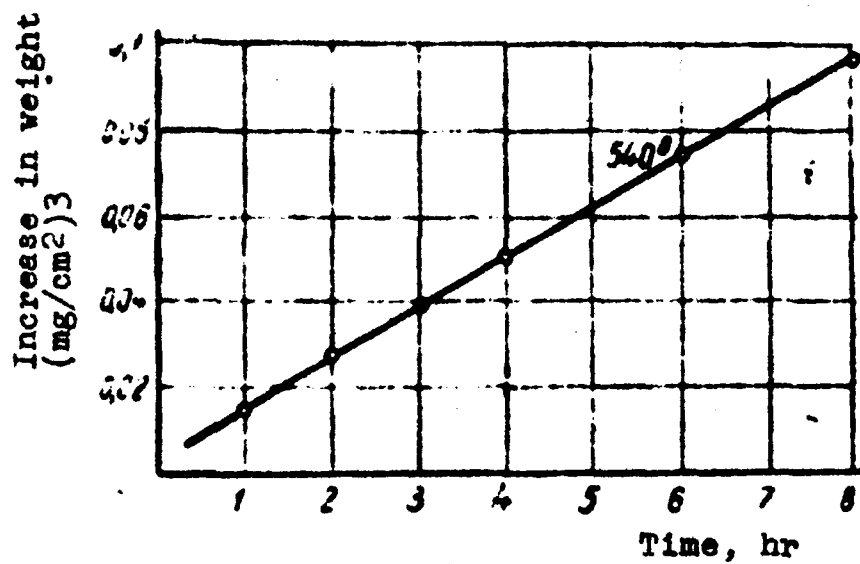
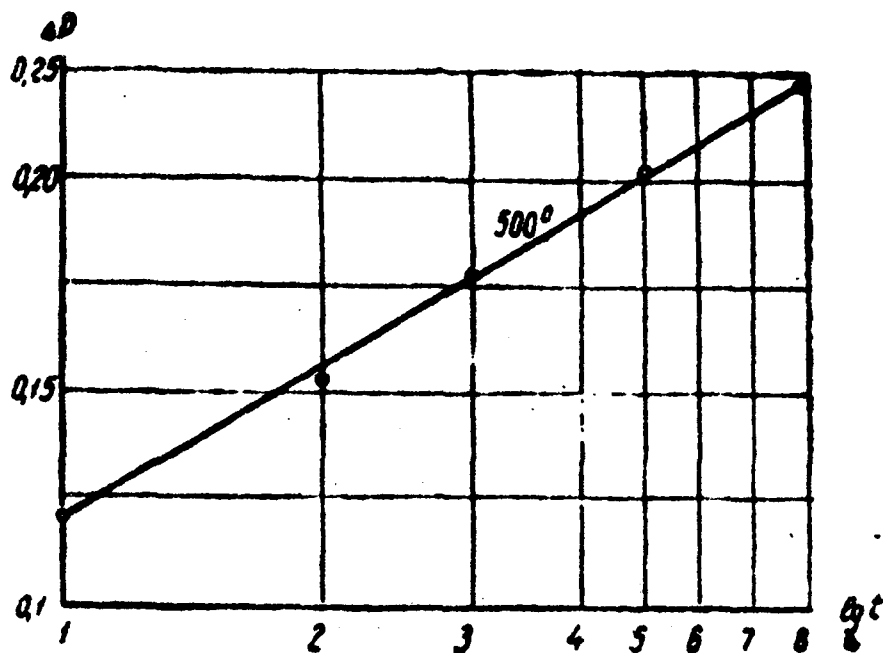


Fig. 5. Graphs corresponding to zirconium oxidation curves of Fig. 4.

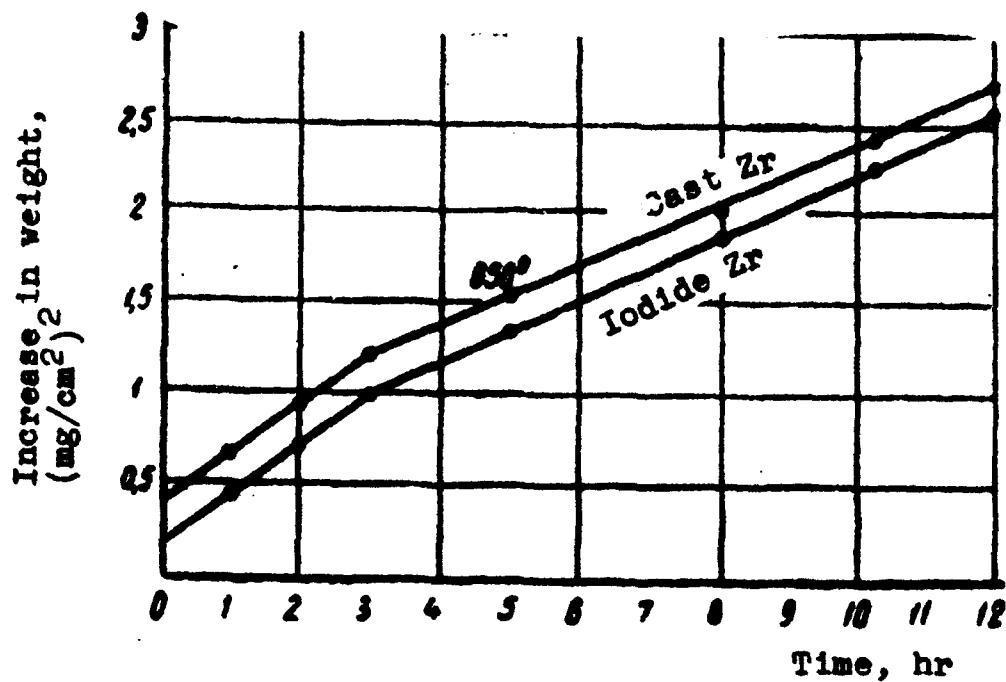
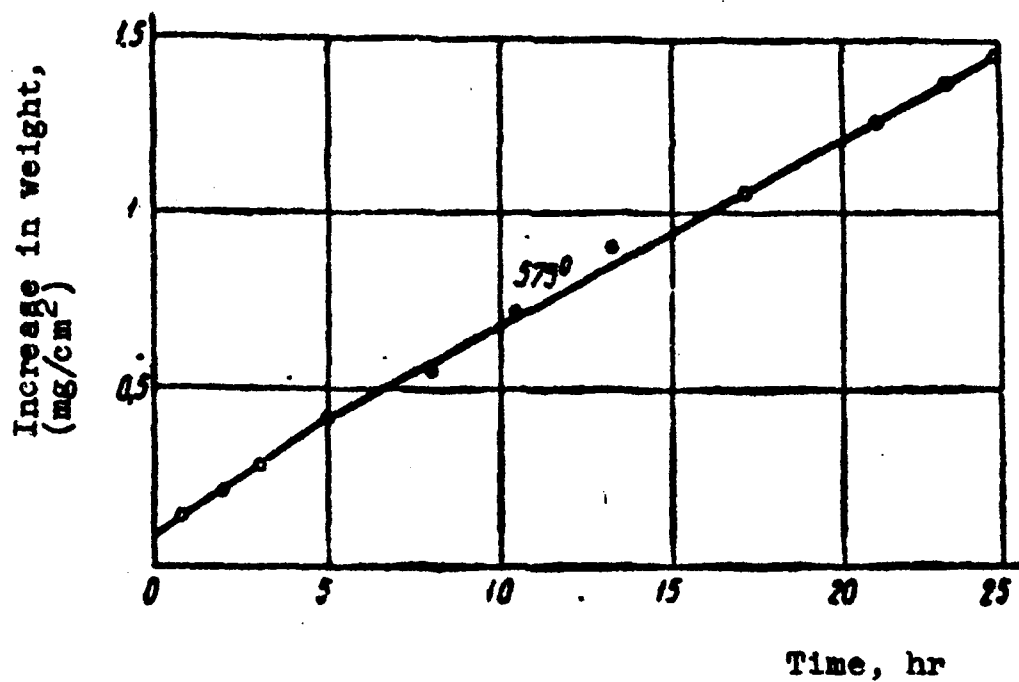


Fig. 5. Graphs corresponding to zirconium oxidation curves of Fig. 4.

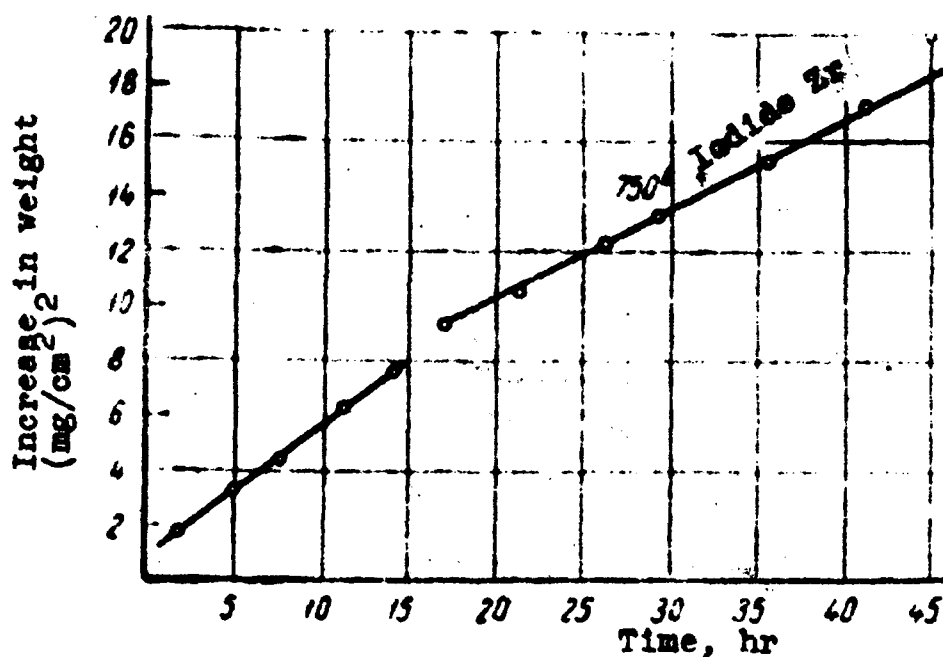
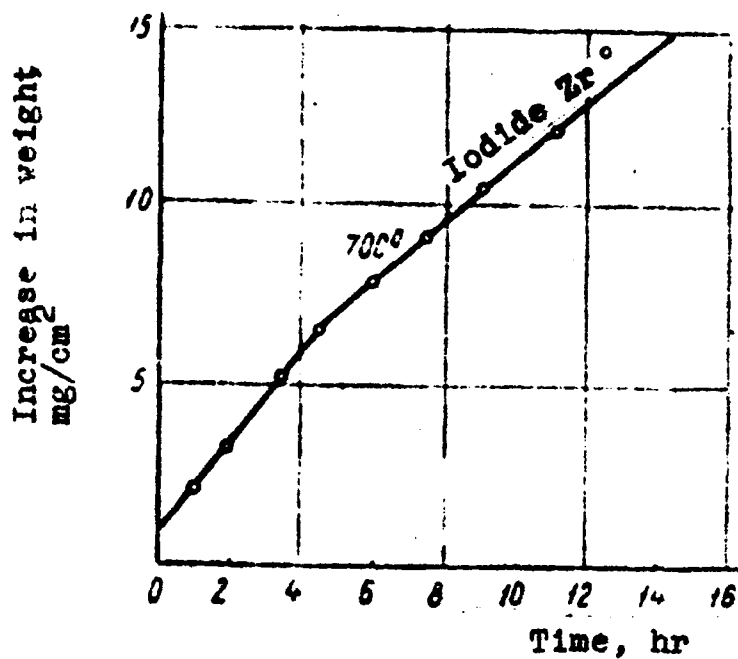


Fig. 5. [continued from pages 18 and 19]
 Graphs corresponding to zirconium
 oxidation curves of Fig. 4.

dized zirconium (Fig. 2b).

The energy of activation, as calculated from the tangent of the slope of the straight plotted line in $\log k - \frac{1}{T}$ coordinates according to k values in the initial oxidation stage (during the first 3 to 5 hours of oxidation) was equal to 29.8 kcal/mol.

However, the existence of these two oxidation stages into the parabolic range is not typical for oxidation of zirconium, although it is for many other metals. Typical of the oxidation kinetics of zirconium (as well as of certain zirconium alloys, as will be shown later) is a stage of accelerated oxidation after the scale has attained the critical thickness. As mentioned before, the value of this thickness depends on the temperature and on the duration of heating. Thus, for instance, for iodide zirconium at 700° this thickness is achieved after 40 hours; at 750°, after 10 hours; and at 800°, after 3 hours.

According to visual observations, the stage of accelerated oxidation begins with the formation of white zirconium oxide at the edges and in several spots on the specimen, whose surface was previously covered with dark blue oxide film. Upon further heating, the white zirconium oxide areas widen and ultimately cover the entire surface of the specimen.

Whereas the dark blue film is solidly attached to the metal and cannot be separated from it, the white film is brittle and porous, and is easily peeled from the surface of the specimen, either whole or in pieces. Electronographic analysis of the oxide structures of the dark blue and white films shows that in the first case the structure is that of tetragonal ZrO_2 , while in the second it is monoclinic. Thus, accelerated zirconium oxidation is linked to the transformation of tetragonal into monoclinic zirconium dioxide.

The dependence of the timing of this transformation on the film thickness of the tetragonal modification at a given temperature, and the decrease in the critical thickness of this film with increasing temperature, as well as the fact that this modification is transformed at lower temperatures than in the case of free thin ZrO_2 films (750°), can all be explained by the influence of constructing stresses formed in the oxide film due to the volume of the oxide which is 1.5 times greater than that of the metal. The mere fact of film formation at low temperatures and in the initial stage of zirconium oxidation at higher temperatures (from 300 to 800°) -- the oxide film consisting of cubic and tetragonal (i.e., metastable) modifications --

as well as the strength of the film's bond with the metal, can probably be explained by P. D. Dankov's /12/ crystallochemical principle: the lattices of cubical and tetragonal modifications correspond better crystallochemically to the α -Zr lattice than to the lattice of monoclinic ZrO_2 . The peeling and cracking of the monoclinic film is explained by and 8% volume increase of this oxide as compared to the volume of tetragonal ZrO_2 , as well as by the different expansion coefficients (that of tetragonal ZrO_2 is 1.5 times greater than that of monoclinic ZrO_2).

It must be noted that the lower rate of oxidation in melted zirconium specimens, as compared with that of iodide zirconium, observed from the moment when tetragonal ZrO_2 is transformed into monoclinic ZrO_2 , is probably caused by admixtures that slow down the transformation of the former modification into the latter.

Conclusions

An electronographic and kinetic investigation of zirconium oxidation, as well as of certain zirconium alloys, was carried out by heating in air over a temperature range of 200 to 800°. The results of this investigation are as follows:

(1) At 270° a thin zirconium film (300-400 Å) is completely oxidized, and the cubic ZrO_2 modification is formed, which is stable up to 650°.

(2) At 650° cubic ZrO_2 is transformed into tetragonal ZrO_2 , stable to 750°; at 750° this is in turn transformed to monoclinic ZrO_2 which is stable to 1300°.

(3) Analogous polymorphic transformations take place in oxide films on massive zirconium heated to between 300 and 800°, but the transformation of tetragonal ZrO_2 into monoclinic ZrO_2 occurs, in this case, only at a certain thickness of oxide film for a given temperature.

(4) Accelerated zirconium oxidation is caused by the tetragonal ZrO_2 into monoclinic ZrO_2 .

(5) The cubic ZrO_2 formed during the heating to 300° of a thin film of zirconium alloy with 5 wt-% Al or 6 wt-% Ti is stable up to 1100°, i.e., the oxides γ - Al_2O_3 and TiO_2 (or TiO) stabilize this modification.

An addition of 15 wt-% Sn to zirconium did not substantially alter the polymorphic transformations of zirconium dioxide heated under the conditions of the preceding experiments.

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Diffusion of Zirconium and Tin in Tin Alloys of Alpha-Zirconium

Following is a translation of an article by G. S. Fedorov, P. I. Zhomov in Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 162-169.⁷

In the article (1) the diffusion of zirconium and tin in β -solid solutions of zirconium and tin was studied. The present communication is the second part of the investigation of tin alloys, and is dedicated to the study of diffusion properties in the range of α -solid solutions of Zr-Sn alloys. As tin solubility in α -Zr is lower than in β -Zr, the alloys under study contained lower quantities of tin -- namely, 0.41, 1.03 and 1.97% Sn -- than those in article (1). Over the temperature range from 820 to 650°, where diffusion coefficients were determined, all the alloys consisted of homogeneous solid solutions.

The alloys were melted in an arc furnace from the same materials as were mentioned in article (1). After melt-forging into rectangular bars and eliminating the oxidized layer on a grinder, the alloys were subjected to a homogenizing anneal under vacuum (10^{-4} mm Hg) at 1100°C for 25 hours. Then the bars were ground for a second time on four sides and cut into separate specimens (approximately 10 X 10 X 18 mm).

A study of the microstructure showed that after cooling from 1100° to room temperature, the alloys acquired a martensite structure as a result of a nondiffusional polymorphic transformation of β -zirconium into α -zirconium. During annealing of the alloys at high temperature (below the temperature of transformation however) diffusion processes and alloy stabilization take place, which in the final analysis must lead to the formation of the usual solid-solution grains. It is quite evident that the distances between grain boundaries in finely crystallized martensite structure are considerably reduced during the process of stabilization. However, it is known that the rate of diffusion is greater along the grain interface in the body of the grain. Therefore, the average diffusion coefficients, which are determined by the method of layers, can undergo considerable change during diffusion annealing if no prior stabilizing annealing is carried out near the temperature of polymorphic transformation. To achieve

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this end specimens were annealed at 820°C for 90 hours.

As in the previous article, radioactive isotopes of zirconium and tin, Zr^{95} and Sn^{113} , were utilized for the determination of diffusion parameters. The isotopes were tested on the specimen in vacuum. The specimens were tied together with their radioactive surfaces facing each other, and then wrapped in molybdenum foil and placed in a quartz ampoule which was welded to a quartz tube. The air was pumped out of the quartz tube to a pressure lower than 10^{-4} mm Hg, whereupon the tube with the ampoule was placed in a furnace and heated for 2-3 hours at a temperature 30° below that of diffusion annealing. Vacuum was maintained during heating by the continuous action of diffusion and prevacuum pumps. Then the ampoule was welded off from the tube. Such preliminary degassing prevented the oxidation of the samples during diffusion annealing.

Diffusion annealing was carried out in a tubular furnace with the temperature automatically regulated to $\pm 3^\circ\text{C}$. The diffusion annealing required hundreds of hours and, at low temperatures, as much as 1,450 hours. The determination of the diffusion coefficient was effected by the method of removing layers and measuring the total radioactivity of the remaining portion of the sample (2).

The results of the investigation are shown in Fig. 1. The values of the activation energies and of the pre-exponential factors D_0 are indicated in Table 1.

The data obtained indicate that the alloying of α -zirconium with tin increases the activation energy of zirconium self-diffusion, and that this increase is approximately proportional to the content of tin in the alloy. Thus the maximum addition of tin (2%) increases the activation energy by 60%. The same effect was observed when β -zirconium was alloyed with tin (1). All this is probably due to the fact that tin addition increases the bonding of zirconium atoms in the lattice of the solid solution. This shows the beneficial influence of tin on zirconium, resulting in the improved mechanical properties of Zr-Sn alloys both at room and at elevated temperatures (3), (4).

The activation energy of α -zirconium self-diffusion, as well as that for β -zirconium, is very low -- 22,000 cal/g-atom. The consolidated graph of the dependence of the self-diffusion coefficient of zirconium on temperature is shown in Fig. 2, which indicates that the presence of tin lowers the self-diffusion coefficient at temperatures below 700°C and, conversely, raises it at higher temperatures.

The diffusion mobility of α -zirconium and of its tin alloys in the range of elevated temperatures differs only

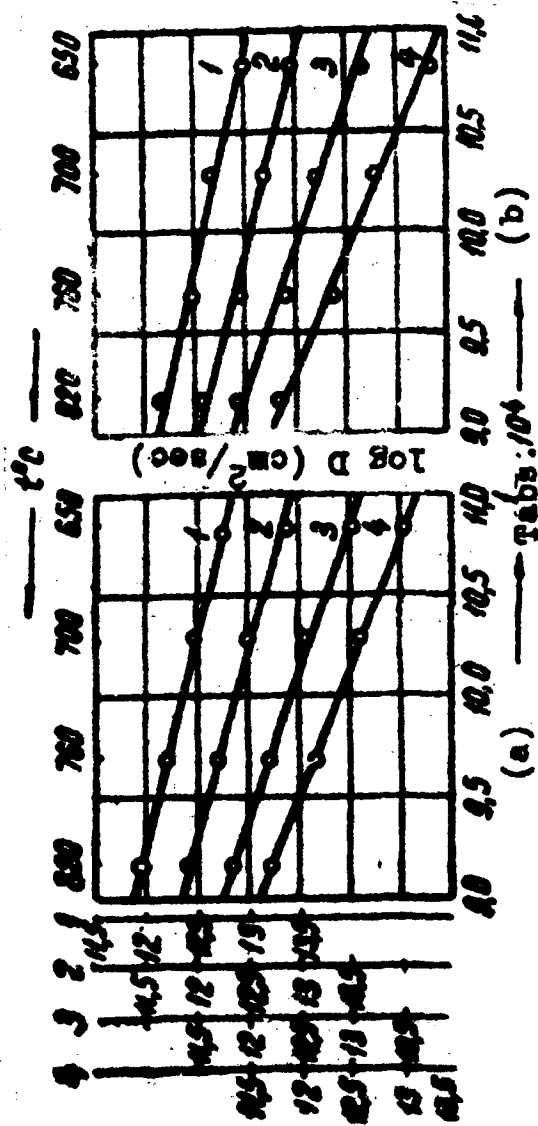


Fig. 1. Results of diffusion study of zirconium (a) and tin (b) in different systems:
 1 - pure Zr; 2 - Zr + 0.41% Sn; 3 - Zr + 1.03% Sn;
 4 - Zr + 1.97% Sn.

Table 1

Diffusing element	Alloy	Q , kcal/g-atom	D_0 , cm^2/sec
Zr	Zr + 0.41% Sn	22	$3 \cdot 10^{-6}$
	Zr + 1.03% Sn	27	$3 \cdot 10^{-7}$
	Zr + 1.97% Sn	32	$2 \cdot 10^{-6}$
	Zr + 1.97% Sn	36	$3 \cdot 10^{-6}$
Sn	Zr + 0.41% Sn	22	$2 \cdot 10^{-8}$
	Zr + 1.03% Sn	24	$5 \cdot 10^{-8}$
	Zr + 1.03% Sn	33	$3 \cdot 10^{-6}$
	Zr + 1.97% Sn	41	$1 \cdot 10^{-4}$

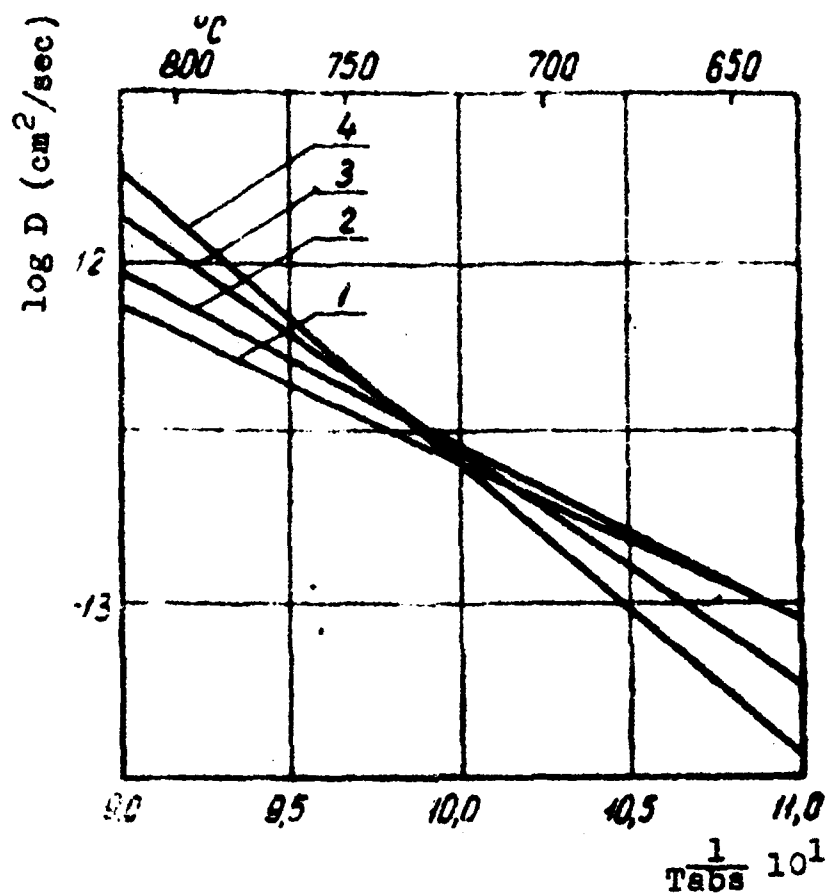


Fig. 2. Consolidated graph of temperature dependence of self-diffusion coefficients of zirconium: pure zirconium (1) and zirconium alloys with 0.41% Sn (2), 1.03% Sn (3) and 1.97% Sn (4).

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slightly from that of the metals of the iron group. In Table 2 are given the self-diffusion coefficients for iron, zirconium and its tin alloy, and nickel, calculated according to formulas of the temperature dependence of the coefficients (1), (2), (5), (6) in the 1000 to 300°C range. From Table 2 it follows that at the temperature of transformation, the self-diffusion coefficient of α -zirconium is seven times greater than the self-diffusion coefficient of nickel whereas it is only 1/40 as large as the α -iron coefficient. At first glance, these facts seem paradoxical if one keeps in mind that the self-diffusion coefficients of β -zirconium at the same temperatures are greater by three orders than the corresponding coefficients of iron-group metals (1). The explanation of such differences is that the polymorphic transformation influences the zirconium and iron self-diffusion coefficients in opposite directions. Indeed, in the transition from γ -iron to α -iron, the coefficients increase 650 times; in the case of the $\beta \rightarrow \alpha$ transformation in zirconium the coefficients of self-diffusion decrease by a factor of 200 (see Table 2).

In connection with the above, the following general rule can be established: a decrease in the diffusion coefficient during polymorphic transformation corresponds to a denser crystal lattice and, conversely, an increase in the coefficients corresponds to a transition from a denser packing to a less dense one. Let us bear in mind that in zirconium the transformation from β to α indicates a transition from body-centered cubic to dense hexagonal packing, while in iron the transition is from face-centered to body-centered cubic.

For this reason, up to 300° one observes approximately the same self-diffusion coefficient in α -Fe and in α -Zr. At lower temperatures, however, owing to the lower value of the activation energy for zirconium self-diffusion, the coefficients for zirconium become greater than those for iron and nickel. At 300° this difference reaches 7 to 9 orders. At such relatively low temperatures, the influence of tin in decreasing the self-diffusion coefficient of zirconium is especially noticeable. From Table 2 one can see that the addition of 2% tin at 300° decreases the coefficient by more than 2 orders.

Alloying of zirconium with tin has the same effect on tin diffusion as was mentioned in the discussion of zirconium self-diffusion. The energy of activation of tin diffusion approximately doubles in an alloy with 2% Sn (Table 1). At temperatures lower than 700°C diffusion coefficients of tin decrease noticeably (Fig. 3).

Table 2

Coefficients of Diffusion, cm ² / sec					
Temperature, °C	γ-Fe	β-Zr	α-Zr	α-Zr+2% Sn	Ni
1000	—	1·10 ⁻¹⁰	—	—	5·10 ⁻¹²
910	2·10 ⁻¹⁰	7·10 ⁻¹⁰	—	—	7·10 ⁻¹²
863	8·10 ⁻¹¹	4·10 ⁻¹⁰	2·10 ⁻¹²	4·10 ⁻¹²	3·10 ⁻¹²
800	1·10 ⁻¹¹	—	1·10 ⁻¹²	2·10 ⁻¹²	4·10 ⁻¹⁴
700	6·10 ⁻¹²	—	4·10 ⁻¹²	3·10 ⁻¹²	2·10 ⁻¹⁵
600	1·10 ⁻¹⁴	—	1·10 ⁻¹²	4·10 ⁻¹⁴	3·10 ⁻¹⁷
500	8·10 ⁻¹⁷	—	2·10 ⁻¹⁴	2·10 ⁻¹⁵	2·10 ⁻¹⁹
400	1·10 ⁻¹⁹	—	2·10 ⁻¹⁵	7·10 ⁻¹⁷	4·10 ⁻²²
300	2·10 ⁻²³	—	1·10 ⁻¹⁶	7·10 ⁻¹⁹	7·10 ⁻²⁶

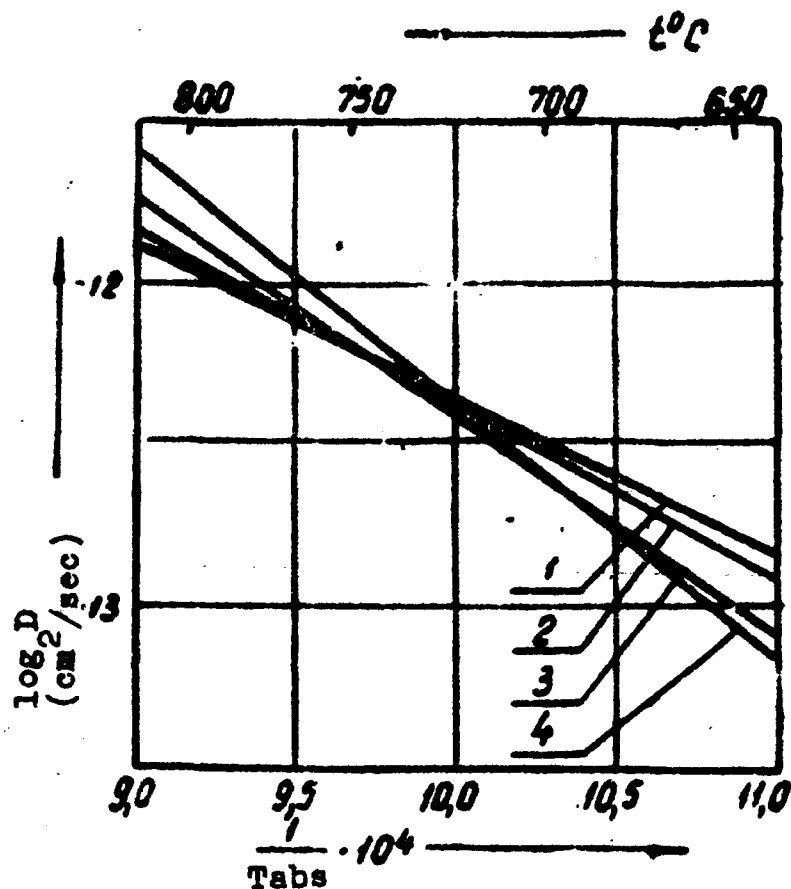


Fig. 1. Consolidated graph of tin diffusion coefficient vs temperature: pure zirconium (1) and zirconium alloys with 0.41% Sn (2), 1.03% Sn (3) and 1.97% Sn (4).

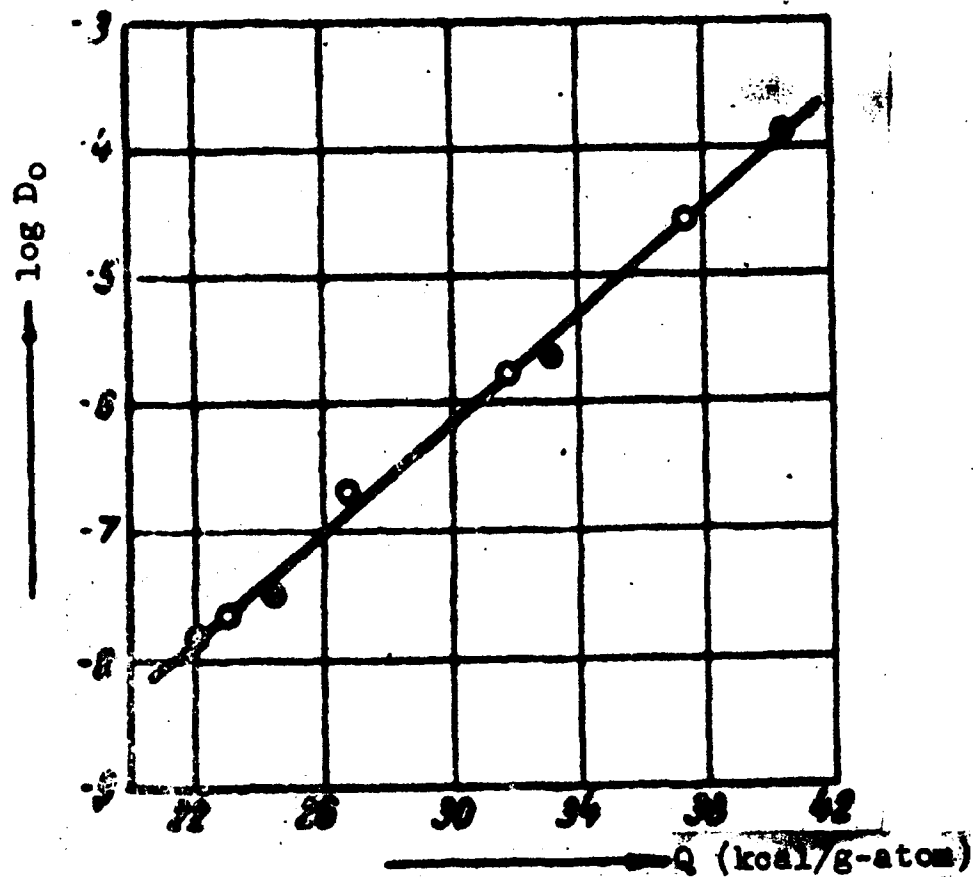


Fig. 4. Graph of the dependence of $\log D_0$ on Q in the diffusion of zirconium and tin into the alloys studied.

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Such an identical influence of tin addition on zirconium self-diffusion and upon tin diffusion is evidently due to the fact that the diffusion through solid-solution crystal lattice by radioactive atoms of zirconium and tin encounters primarily zirconium atoms, as the number of tin atoms in the solid solution is very low (not more than 2%). The strengthening of the bonds in the zirconium solid solution results in an increase in the activation energies of Zr self-diffusion and of tin diffusion.

The results of the study establish a connection between the pre-exponential factor D_0 and the activation energy of diffusion in the following relation: $D_0 = 2 \times 10^{-13} e^{Q/2000}$ (Fig. 4). It differs from the dependence established for β -zirconium alloys, owing apparently, to the difference in the crystalline structures of α - and β -zirconium.

The activation energies of zirconium self-diffusion and tin diffusion, as obtained in our work, confirm the published data (7) and (8). However, the pre-exponential factors D_0 are lower than the published ones by one or two orders. This may be due to the fact that in the present work specimens were subjected to long annealing at temperatures near the temperature of polymorphic transformation (to stabilize their structure) and, in addition, more perfect methods of coating the specimens with radioactive isotopes, mainly by dusting under vacuum, were applied.

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Diffusion of Zirconium and Tin in Tin Alloys of Beta-Zirconium

Following is a translation of an article by G. B. Fedorov and V. D. Gulyakin in Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 170-178.⁷

Zirconium is one of the most promising structural materials for the building of reactors. It satisfies stringent requirements of small capture cross section for thermal neutrons and high corrosion resistance, and, it has adequate mechanical properties at elevated temperatures. Hence great attention is being paid to zirconium and its alloys /1/, /2/. Especially prominent are the desirable properties of zirconium alloys with tin, in particular Zircalloy-2 /3/, /4/. However, while there are fairly detailed studies of the corrosion behavior, the mechanical and general physical properties of zirconium and its tin alloys, and their diffusion characteristics, are practically unexplored. A knowledge of diffusion parameters is important in understanding the processes taking place in alloys at high temperatures and, in particular, the weakening process /5/.

The present article is the first in a set of diffusion process studies of zirconium and its tin alloys. The aim of the work was to study the mobility of zirconium and tin atoms in pure zirconium, and the influence of tin addition on diffusion constants in β -solid solution of zirconium and tin. The alloys contained 0.7, 3.25 and 5.6% Sn and within the temperature range studied they were homogeneous solid solutions /1/, as was confirmed by metallographic investigation. The alloys were melted from iodide zirconium rods (hafnium content 0.7%) and tin (99.9% pure). Melting was done in an MIFI-9-3 arc furnace in an atmosphere of purified argon. Each melt was repeated 4 or 5 times for a more uniform distribution of tin. Thereafter, the ingots were subjected to rapid induction heating by high frequency current and then they were forged in air into bars of rectangular cross section (10 X 8 mm). The oxidized layer was removed on a grinder. Later, these bars were subjected to a homogenizing anneal under vacuum (10^{-4} mm Hg) at 1120° for 20 hours, after which they were again polished and cut into separate specimens.

The study of diffusion characteristics was carried

out with the aid of artificial radioactive isotopes Zr^{95} and Sn^{113} by the method of removing layers and measuring the total radioactivity of the remaining part of the specimen, as proposed by Gruzin /6/. One side of the specimen was coated with the radioactive substance by dusting under vacuum. This layer had a thickness of a few hundredths of a micron and registered 1000-2000 counts per minute on a γ -counter. A radiographic study confirmed our supposition that the substance uniformly coated the entire surface of the specimen.

The specimens studied were tied in pairs with molybdenum wire with the radioactive surfaces meeting, and then were wrapped in molybdenum foil and placed in a quartz tube. Diffusion annealing was done in a tubular furnace while the continuous working of diffusion and prevacuum pumps maintained a vacuum of 10^{-4} mm Hg in quartz tubes. The temperature was regulated to $\pm 3^{\circ}C$. The annealing lasted for several hours.

The results of the investigation are represented graphically in Fig. 1. Data concerning self-diffusion of zirconium in the β -solid solution stage indicates that the addition of tin considerably increases the energy of activation Q (Table 1); this increase apparently is caused by stronger bonding of the zirconium atoms in the solid-solution crystal lattice. Thus 0.7% Sn increases the self-diffusion energy of activation by 40%. With further alloying with tin, the increase is less pronounced, but nevertheless, at 5.6% Sn, the heat of dissociation has increased to 50,000 cal/g-atom. As is evidenced by the graph of temperature vs self-diffusion factor (Fig. 2), an increase in tin content regards diffusion processes in alloys. The greatest influence of tin addition on the mobility of zirconium atoms is exercised in the low-temperature range of the β -phase. At 1000° , an addition of 5.6% tin decreases zirconium self-diffusion from 2×10^{-9} cm²/sec to 4×10^{-10} cm²/sec. At 1200° diffusion coefficients for all alloys become more or less the same, and at temperatures above 1200° , the tin begins to promote the self-diffusion of zirconium. If one assumes that in alloys of similar type diffusion coefficients at the melting point must be approximately the same, then in our case one must conclude that upon addition of tin, the melting points of the alloys must decline. This actually occurs, as is evident from the Zr-Sn state diagram /1/. The same dependence was observed by us earlier for nickel-chromium alloys /5/. Apparently, in binary systems that form solid solutions of limited solubility, when an increase in the amount of the dissolved element decreases

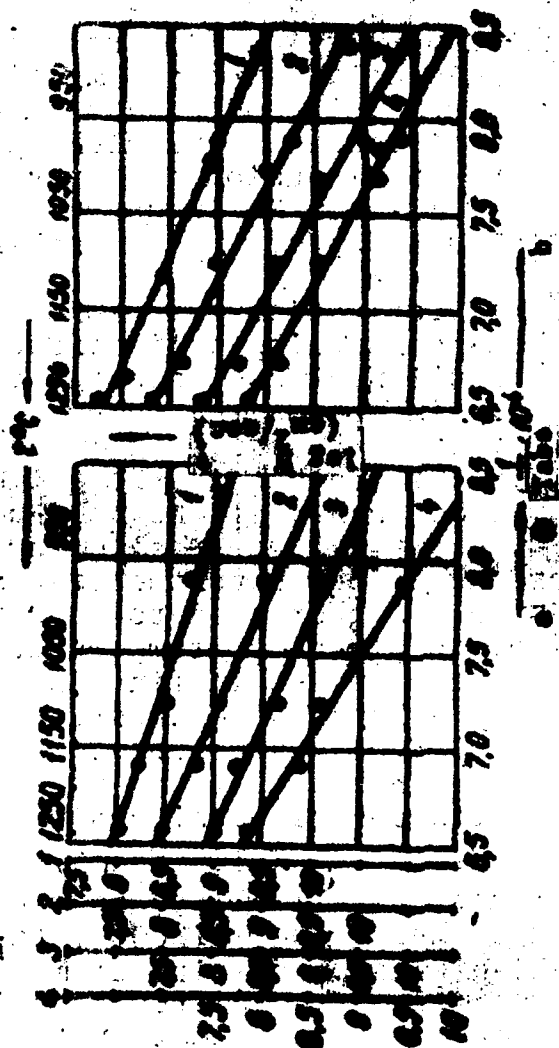


Fig. 1 Results of diffusion of zirconium (a) and tin (b) in systems:
 1 - pure Zr; 2 - Zr + 0.7% Sn; 3 - Zr + 3.25% Sn;
 4 - Zr + 5.6% Sn.

Table 1

Element diffusing	Alloy	Q, kcal/g-atom	D_0 , cm ² /sec
Zr	Zr + 0,7% Sn	26	$4 \cdot 10^{-3}$
	Zr + 3,25% Sn	36	$2 \cdot 10^{-3}$
	Zr + 5,6% Sn	39	$3 \cdot 10^{-3}$
		50	$2 \cdot 10^{-1}$
Sn	Zr + 0,7% Sn	39	$5 \cdot 10^{-3}$
	Zr + 3,25% Sn	43	$2 \cdot 10^{-2}$
	Zr + 5,6% Sn	50	$2 \cdot 10^{-1}$
		52	$4 \cdot 10^{-1}$

the melting point of the alloy (analogous to the β -phase of the Zr-Sn diagram), the energy of activation of diffusion must increase with the rate of alloying. However, this conclusion requires additional study.

Attention is drawn to the very low magnitude of the activation energy of zirconium self-diffusion (26 kcal/g-atom) which does not correspond to the high melting point of zirconium. Usually, the self-diffusion of metals follows Bulgakov's rule [9]; $Q = 40 T_s$, where T_s is the absolute melting point. In the case of zirconium this relationship does not hold (Table 2); at the same time, for other refractory metals such as Ni [10], Co [11] and Mo (according to data of the investigation by one of the authors of the present work conjointly with Gruzin, Pavlinov and Tyutyunnik -- in this collection), this relationship is true as is the approximate equality of the activation energy of self-diffusion Q to two-thirds the sublimation energy S . However, the activation energy of zirconium self-diffusion is only a small portion of the sublimation energy, namely, one-fourth of it (Table 2). Furthermore, we must note a very high mobility of zirconium atoms as compared to the mobility of atoms of the above-mentioned metals. As it appears from Table 3, self-diffusion coefficients of zirconium in the low-temperature range of the β -phase are higher by three orders than the self-diffusion coefficients of nickel and cobalt. Moreover, one must take into consideration that the melting point of zirconium is approximately 300° higher than that of nickel and cobalt. This evidently explains the marked increase in the size of the grain in the β -phase, as mentioned in the literature [3].

If one compares zirconium with the more refractory metal molybdenum, the difference in diffusion coefficients is seen to be a great deal larger -- by a factor of 10 billion (Table 3). However, this comparison refers to the lower limit of the β -zirconium range. If one compares the self-diffusion coefficient at the melting points of the above-mentioned metals, the difference between the coefficients decreases by as much as one order. Apparently, for zirconium as well as for other metals, the self-diffusion coefficient at the melting-point temperature characterizes the limit mobility of atoms in the solid body (10^{-9} to 10^{-8} cm²/sec).

The magnitude of the pre-exponential factor of zirconium self-diffusion $D_0 = 4 \cdot 10^{-5}$ cm²/sec, is very low compared with usual D_0 values of self-diffusion in metals. An analysis of literature data indicates that the magnitudes of pre-exponential factors of self-diffusion of different metals differ relatively little one from the other, and

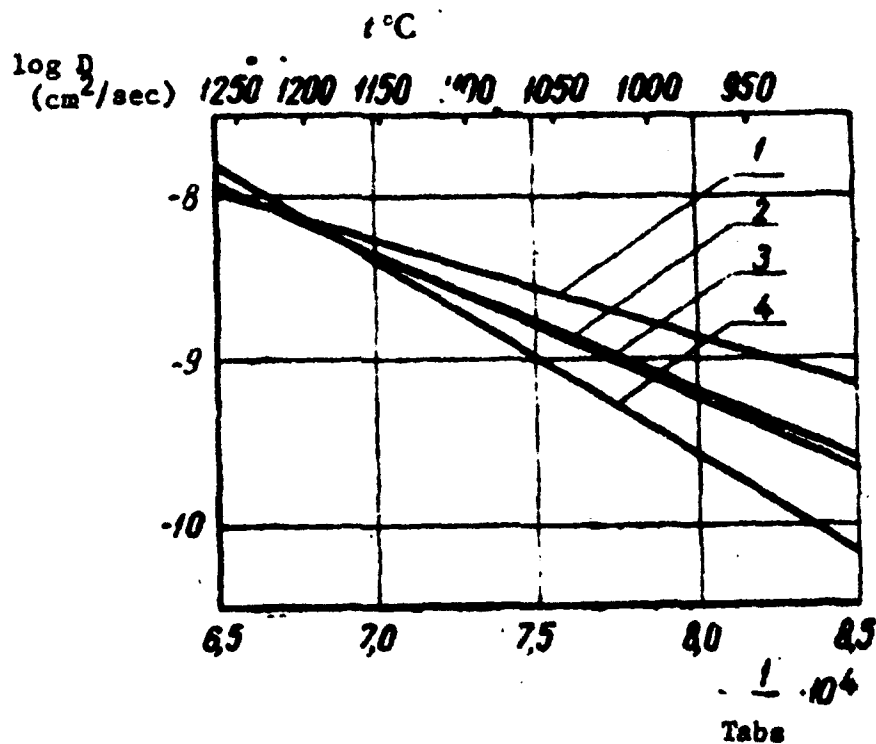


Fig. 2. Consolidated graph of temperature vs zirconium self-diffusion zirconium in Zr alloys with 0.7% Sn (2), 3.25% Sn (3) and 5.6% Sn (4); the straight line (1) is for pure zirconium.

Table 2

Metals	Q , cal/g-atom	Melting point, $^{\circ}\text{C}$	$40\ T_0$, $^{\circ}\text{K}$	S , cal/g-atom	$\kappa = Q/S$
Ni	66 800	1455	69 100	85 000	0,78
Co	62 000	1490	70 600	95 000	0,65
Mo	114 000	2620	116 000	160 000	0,75
Zr	26 000	1830	84 000	110 000	0,24

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Table 3

Temperature, °C	Ni	Co	Mo	Zr
900	$7 \cdot 10^{-12}$	$7 \cdot 10^{-13}$	$3 \cdot 10^{-12}$	$6 \cdot 10^{-12}$
1100	$1 \cdot 10^{-11}$	$3 \cdot 10^{-11}$	$4 \cdot 10^{-11}$	$3 \cdot 10^{-11}$
1300	$8 \cdot 10^{-12}$	$6 \cdot 10^{-12}$	$7 \cdot 10^{-12}$	$1 \cdot 10^{-11}$
1500		--	$1 \cdot 10^{-11}$	$3 \cdot 10^{-11}$
1700		--	$1 \cdot 10^{-12}$	$5 \cdot 10^{-11}$
$t_{m.p.}$	$5 \cdot 10^{-12}$	$5 \cdot 10^{-12}$	$1 \cdot 10^{-11}$	$8 \cdot 10^{-11}$

are within the limits of $2 \cdot 10^{-1} \div 5 \text{ cm}^2/\text{sec}$. ^{*)} One can show that this is a consequence of the closeness of self-diffusion coefficients at the melting point of metals, and of the above-mentioned relation between the melting point and the self-diffusion energy of activation. Indeed, if the quantities and relations mentioned above are introduced into the equation of temperature vs diffusion coefficient, it is found that:

$$10^{-9} \div 10^{-8} = D_0 e^{-\frac{4075}{Rt_s}}$$

whence $D_0 = 5 \cdot 10^{-1} \div 5 \text{ cm}^2/\text{sec}$, which is in good agreement with experiments. For zirconium, however, the pre-exponential factor of self-diffusion is less by four to five orders. The addition of tin also increases the activation energy of tin diffusion in β -solid solution of zirconium (Table 1) although this increase is somewhat lower than that for zirconium self-diffusion. Thus, 5.6% Sn increases the Q of zirconium self-diffusion by 24,000 cal/g-atom, while increasing the Q of tin

^{*)} This difference is small, as compared to the difference between the self-diffusion factors (Table 3).

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diffusion by only 13,000 cal/g-atom. The activation energy of Zr and Sn diffusion in the solid solutions studied can be represented as a graph (Fig. 3). The variation of the diffusion coefficient of tin with tin content in zirconium alloys has the same characteristics as the variation of the coefficient of zirconium self-diffusion (Fig. 4). The results obtained by us for zirconium self-diffusion and tin diffusion in zirconium are in agreement with data in articles /7/ and /8/.

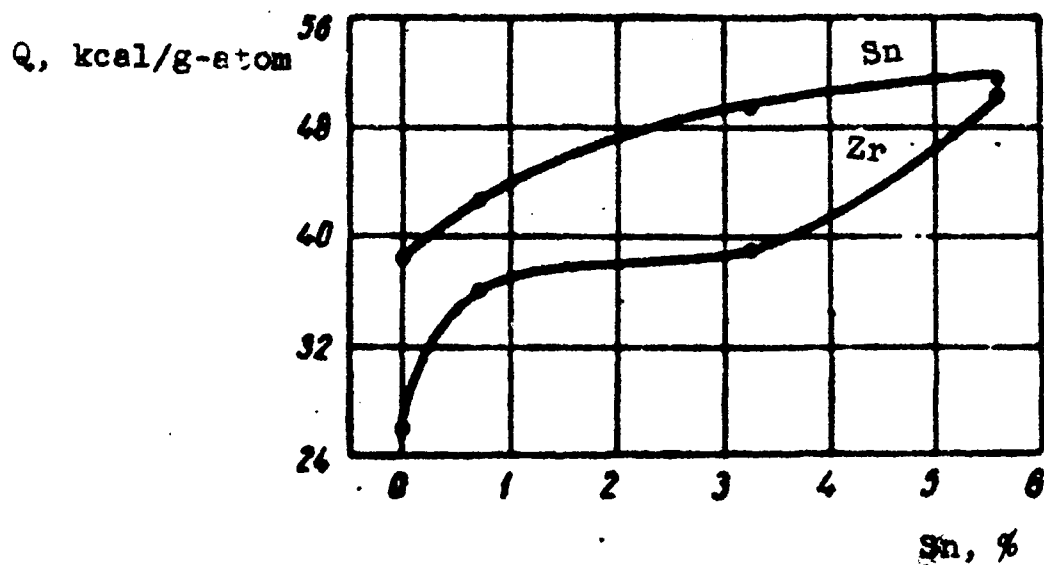


Fig. 3. Dependence of activation energy of zirconium and tin diffusion on the content of tin in zirconium alloys.

It is interesting to note that from works /5/, /12/, /13/, as well as according to data obtained by us, one can establish a relation between the pre-exponential factor and the activation energy of diffusion: $D_0 = A e^{Q/B}$. Therefore the graph of $\log D_0$ vs Q will be a straight line (Fig. 5). In Table 4 numerical values for the coefficients A and B are given according to both the results of the present work, and the data in /5/, /12/, /13/. It appears that in alloys formed by substitution in Ni, Fe and Co solid solutions, the magnitudes of these coefficients are practically identical. For diffusion of carbon in ferrite (solid solution formed by penetration) the coefficients have substan-

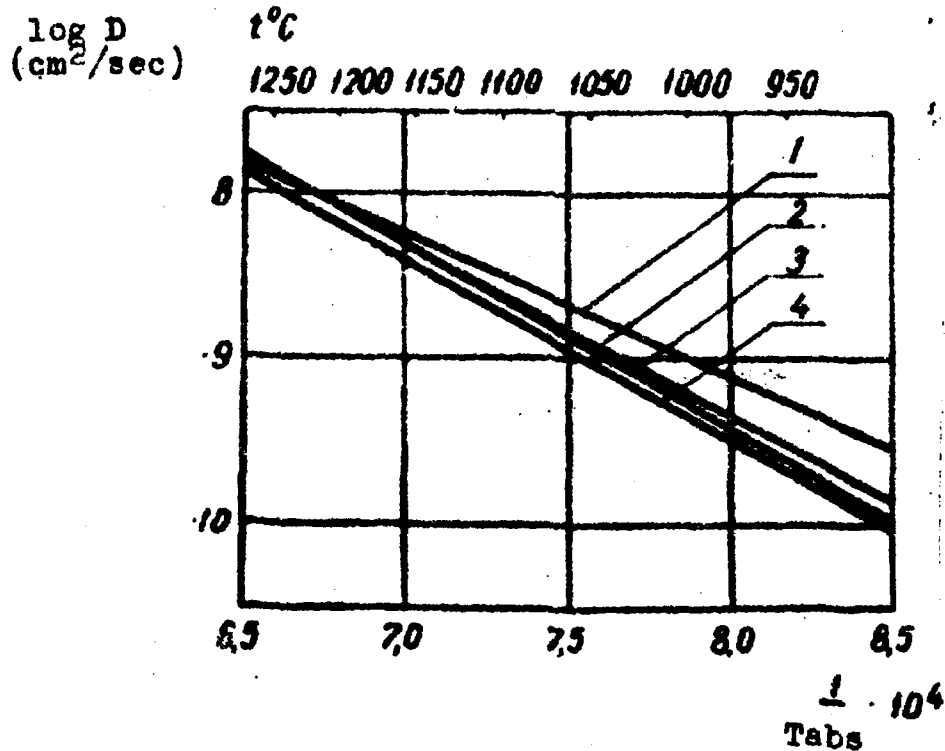


Fig. 4. Consolidated graph of temperature vs tin diffusion in pure zirconium (1) and in zirconium alloys with 0.7% Sn (2), 3.25% Sn (3) and 5.6% Sn (4).

Table 4

Material in which diffusion takes place	Diffusing element	Type of solid solution	A	B
Al alloys	Cr	substitution	$2 \cdot 10^{-10}$	2900
Fe and Co alloys	Fe, Co, Cr, W	"	$3 \cdot 10^{-10}$	3030
C alloys	C	penetration	$3 \cdot 10^{-7}$	1820
Zr alloys	Zr and Sn	substitution	$3 \cdot 10^{-9}$	2810

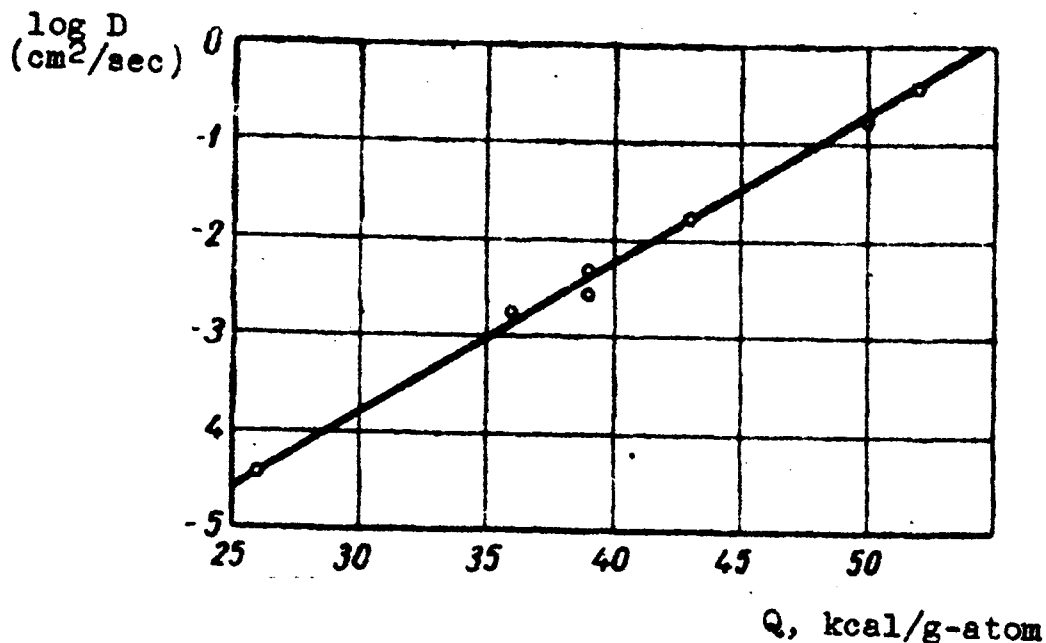


Fig. 5. $\log D_0$ vs Q for diffusion of Zr and Sn into the alloys studied.

tially different values. Apparently this indicates a difference in the mechanics of diffusion. The magnitudes of coefficients A and B in zirconium alloys differ but slightly from the first two relations indicated in Table 4.

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